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PATENT APPLICATION

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11/04/98

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VERIFIED

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TITLE

SOLID ELECTROLYTIC CAPACITOR AND METHOD FOR PRODUCING THE SAME

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Attn: Assistant Commissioner for Patents, Washington, DC 20231

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53(c).

Docket Number	P52248	Type a plus sign (+) inside this box -->	+

INVENTOR(s)/APPLICANT(s)

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TITLE OF THE INVENTION (280 characters max)

SOLID ELECTROLYTIC CAPACITOR AND METHOD FOR PRODUCING THE SAME

CORRESPONDENCE ADDRESS

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X Specification* *Japanese Language ___ Drawing(s)	*Number of Pages* 14 *Number of Claims* 5 *Number of Sheets* 0	___ Small Entity Statement ___ Other (specify)

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X A check or money order is enclosed to cover the Provisional Application filing fees. The Office is also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. ___ The Commissioner is hereby authorized to charge filing fees and/or credit any difference or overpayment to Deposit Account No. 19-4880.	Provisional Application Filing Fee Amount $150.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

X No.

___ Yes, the name of the U.S. Government agency and the Government contract number are: ___

Respectfully submitted, Waddell A. Biggart	Date: November 4, 1998
Waddell A. Biggart Type or Printed Name	Registration No. 24,861

___ Additional inventors are being named on separately numbered sheets attached hereto.

PROVISIONAL APPLICATION FILING ONLY

【書類名】　　　　明細書

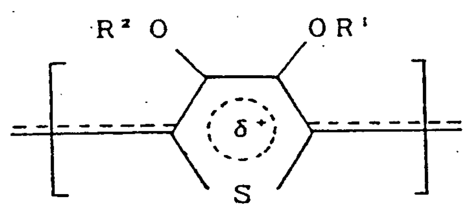
【発明の名称】　　固体電解コンデンサ及びその製造方法

【特許請求の範囲】

【請求項１】　表面に誘電体酸化皮膜を形成した弁作用金属陽極箔上に固体電解質として、導電性ポリチオフェン組成物を設けた固体電解コンデンサの製造方法において、該組成物中の硫酸イオン含量が０．１～１０重量％の範囲であり、かつナフタレンスルホン酸イオン含量が１～５０重量％の範囲であることを特徴とする固体電解コンデンサ。

【請求項２】　請求項１記載の導電性ポリチオフェン組成物中に、下記一般式（Ｉ）

【化１】



（Ｉ）

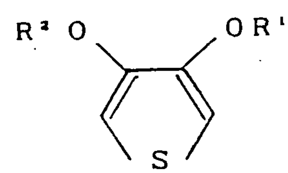
（式中、置換基R^1及びR^2は、各々独立に水素または炭素数１～６の直鎖状もしくは分岐状の飽和もしくは不飽和のアルキル基、もしくは炭素数１～６の炭化水素基が互いに任意の位置で結合して、式中記載の２つの酸素元素を含む少なくとも１つ以上の５乃至７員環の飽和炭化水素の環状構造を形成する置換基を表わす。また、前記環状構造を形成する範囲には、置換ビニレン基または置換ｏ－フェニレン基等の化学構造が含まれる。δは０～１の範囲である。）で表わされる構造単位を含むことを特徴とする固体電解コンデンサ。

【請求項３】　請求項１記載の硫酸イオンが、過硫酸塩の還元体を起源とすることを特徴とする固体電解コンデンサ。

【請求項４】　表面に誘電体酸化皮膜を形成した弁作用金属陽極箔上に固体電解質として、導電性ポリチオフェン組成物を設けた固体電解コンデンサの製造

方法において、下記一般式（II）

【化２】



（II）

（式中、置換基R^1、R^2は、前記請求項１記載の範囲である）
で表わされるチオフェンモノマーを、ナフタレンスルホン酸アニオンの共存下で過硫酸塩の作用によって酸化重合させて該固体電解質を製造することを特徴とする請求項１記載の固体電解コンデンサの製造方法。

【請求項５】　請求項４記載の過硫酸塩が、過硫酸アンモニウムまたは過硫酸カリウムであることを特徴とする固体電解コンデンサの製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】

本発明は、耐電圧特性に優れた固体電解コンデンサ及びその製造方法に関するものであり、詳しくは該固体電解質の製造方法において、特定のチオフェン化合物の重合反応がナフタレンスルホン酸アニオンの共存下で、過硫酸塩を酸化剤として重合させる方法を有する固体電解コンデンサの製造方法及び該コンデンサに関するものである。

【０００２】

【従来の技術】

固体電解コンデンサは、エッチング処理された比表面積の大きな金属箔からなる陽極基体に、誘電体の酸化皮膜層が形成され、この外側に対向する電極として固体の半導電体層（以下、固体電解質と略する）が形成され、そして望ましくは

さらに導電ペーストなどの導電体層が形成され、該コンデンサの基本素子が作製される。次いで、素子全体がエポキシ樹脂等で完全に封止され、コンデンサ部品として幅広く電気製品に使用されている。

【０００３】

このうち、固体電解質には、従来から例えば、二酸化マンガンや二酸化鉛等の無機半導体材料、ＴＣＮＱ錯塩、または電導度が10^{-3}～5×10^{3} Ｓ／ｃｍの範囲である真性導電性高分子（特開平１－１６９９１４号公報）やπ共役系のポリアニリン（特開昭６１－２３９６１７号公報）、ポリピロール（特開昭６１－２４０６２５号公報）、ポリチオフェン誘導体（特開平２－１５６１１号公報）等の使用が知られている。

【０００４】

また固体電解質の形成方法については、従来から細孔あるいは空隙構造を有する弁作用金属表面の誘電体層上に固体電解質層を融解して形成する方法や誘電体層上で導電性高分子の固体電解質を産生する方法等が知られている。例えば、ピロールやチオフェン等の複素五員環式化合物の重合体を使用する場合、陽極箔を複素五員環式化合物を低級アルコールと水からなる溶液に溶解した液に浸漬した後、酸化剤と電解質を溶かした水溶液に浸漬して化学重合させ、導電性化合物を形成する方法（特開平５－１７５０８２号公報）、３，４－ジオキシエチレンーチオフェンモノマー及び酸化剤を好ましくは溶液の形態において、前後して別々にまたは一緒に金属箔の酸化被覆層に塗被して形成する方法（特開平２－１５６１１号公報）等が知られている。

【０００５】

チオフェン等の複素五員環式化合物を化学重合できる酸化剤には、塩化鉄（III)、$Fe(ClO_4)_3$や有機酸鉄（III)、無機酸鉄（III)、アルキル過硫酸塩、過硫酸アンモニウム（以下、ＡＰＳと略す）、過酸化水素、$K_2Cr_2O_7$等が開示されている（特開平２－１５６１１号公報）。

【０００６】

【発明が解決しようとする課題】

しかしながら、前記二酸化マンガンを用いた固体電解質のコンデンサーは、硝

酸マンガンの熱分解時に酸化皮膜層が破壊されてしまう欠点があり、またインピーダンス特性も不十分であった。二酸化鉛を用いる場合は、環境上への配慮の心配もあり好ましくなかった。ＴＣＮＱ錯塩を使用する固体電解質のコンデンサは、熱溶融加工性や導電性に優れているが、ＴＣＮＱ錯塩自体の耐熱性に問題がありハンダ耐熱性の信頼性が悪かった。これらの欠点を改善するために、前記ポリピロール等の導電性高分子が電解重合法または化学的重合法によって誘電体表面の固体電解質に適用されたが、皮膜の均一性やハンダ耐熱性、インピーダンス特性等が充分とは言えなかった。

このように、実用上のコンデンサー素子を製造するにあたり、固体電解質の材料選定はもちろん、電導度の熱的安定性、皮膜の均一性等の制御が重要であり、チオフェン類の化学重合法においては酸化剤の種類や残量あるいはその酸化剤還元体の残量、他のドーパント能を有するアニオンの含量、あるいは残存モノマーの洗浄方法等も重要な技術課題である。

【０００７】

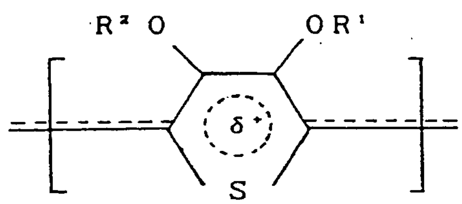
【課題を解決するための手段】

本発明は、最小軽量、高容量、高周波特性、ｔａｎδ、漏洩電流、耐熱性（リフロー性）や耐久性等の要求に対して優れた固体電解コンデンサを製造することを目的に、酸化剤の種類、酸化剤還元体の残量、ドーパント能を有するアニオン種と含量等について鋭意検討を重ねた結果、表面に誘電体酸化皮膜を形成した弁作用金属陽極箔上に、固体電解質として導電性ポリチオフェン組成物を設けた固体電解コンデンサの製造方法において、該組成物中の硫酸イオン含量が０．１～１０重量％の範囲であり、かつナフタレンスルホン酸イオン含量が１～５０重量％の範囲であることを特徴とする固体電解コンデンサおよびその製造方法を提供して、前記課題を解決した。特に、本発明の固体電解コンデンサによって前記目的の要求性能の他に、耐電圧特性の優れたコンデンサを製造することが可能となった。

【０００８】

即ち、前記導電性ポリチオフェン組成物中に、下記一般式（Ｉ）

【化３】



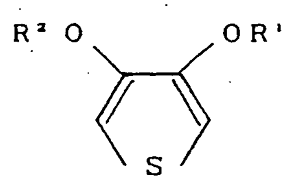
（Ｉ）

（式中、置換基R^1及びR^2は、各々独立に水素または炭素数１～６の直鎖状もしくは分岐状の飽和もしくは不飽和のアルキル基、もしくは炭素数１～６の炭化水素基が互いに任意の位置で結合して、式中記載の２つの酸素元素を含む少なくとも１つ以上の５乃至７員環の飽和炭化水素の環状構造を形成する置換基を表わす。また、前記環状構造を形成する範囲には、置換ビニレン基または置換ｏ－フェニレン基等の化学構造が含まれる。δは０～１の範囲である。）で表わされる構造単位を含むことを特徴とする固体電解コンデンサを提供する。

【０００９】

前記固体電解コンデンサは、詳しくは前記導電性ポリチオフェン組成物を設けた固体電解コンデンサの製造方法において、下記一般式（II）

【化４】



(II)

（式中、置換基R^1、R^2は、前記一般式（Ｉ）記載の範囲である。）

で表わされるチオフェンモノマーを、ナフタレンスルホン酸アニオンの共存下で過硫酸塩の作用によって酸化重合させて該固体電解質を製造することを特徴とするものであり、耐電圧特性に優れた低インピーダンスな固体電解コンデンサを製造することができ、本発明に至った。

【００１０】

以下、本発明を詳細に説明する。

本発明は、前記製造方法において、対向する電極と一方の電極表面に金属酸化物の微細構造からなる誘電体層及びその誘電体層上に、前記一般式（II）で示される特定のチオフェン類を化学重合して得られる導電性重合体組成物を固体電解質に使用するものであり、前記一般式（II）中のR^1及びR^2は、各々独立に水素または炭素数１～６の直鎖状もしくは分岐状の飽和もしくは不飽和のアルキル基を表し、好ましい置換基は、メチル、エチル、プロピル、イソプロピル、ビニル、アリルが挙げられる。さらに、R^1及びR^2の炭素数１～６の炭化水素基が互いに任意の位置で結合して、前記一般式（II）中記載の２つの酸素元素を含む、少なくとも１つ以上の５乃至７員環の飽和炭化水素の環状構造を形成する置換基であり、例えば、１，２－エチレン、１，２－プロピレン、１，２－ジメチル－エチレンが好ましい。また、R^1及びR^2は、前記、炭素数１～６の炭化水素基が互いに任意の位置で結合して、置換ビニレン基または置換ｏ－フェニレン基等の不飽和炭化水素の環状構造を形成してもよく、例えば、１，２－ビニレン、１，２－プロペニレン、２，３－ブチレン２－エン、１，２－シクロヘキシレン、メチル－ｏ－フェニレン、１，２－ジメチル－ｏ－フェニレン、エチル－ｏ－フェニレンが挙げられる。

【００１１】

本発明の製造方法において使用される、前記一般式（II）のチオフェン類のうち、３，４－ジオキシエチレン－チオフェンをはじめとする一部の単量体化合物は、公知（特開平２－１５６１１号公報）であり、本発明で使用する過硫酸塩の酸化剤のうち、過硫酸アンモニウム（ＡＰＳと略する）やアルカリ金属過硫酸塩の使用も公知である。

しかしながら、本発明は導電性組成物中の硫酸イオン含量が０．１～１０重量

%の範囲であり、好ましくは０．２～５重量％であり、かつナフタレンスルホン酸イオン含量が１～５０重量％の範囲であり、好ましくは５～４０重量％であることを特徴とし、かつ導電性組成物中に前記一般式（Ｉ）で表わされる構造単位を含む重合体を含む固体電解質を具備した固体電解コンデンサは、耐電圧特性に特に優れたものでありこれまで知られていなかった。さらに本発明は、前記硫酸イオン含量とナフタレンスルホン酸イオン含量の総計値が、導電性組成物の全重量に対して、１．１～６０重量％の範囲であることが好ましい。

【００１２】

通常、コンデンサの製造方法において、高容量の高周波特性並びにｔａｎδ、漏洩電流、耐熱性（リフロー性）、耐久性等を改善するためには、前記固体電解質の形成方法が重要である。そのためには、固体電解質を密に充填形成して導電パスの均一性を改善することは重要であり、導電性組成物の構成が非常にコンデンサ特性に影響を与える。本発明においては、前記チオフェンモノマーをナフタレンスルホン酸アニオンの共存下で、過硫酸塩の作用によって酸化重合させて該固体電解質を製造する工程を、１つの陽極基板に対して複数回、好ましくは５～２０回繰り返すことによって容易に達成することができる。この場合、前記チオフェンモノマーとナフタレンスルホン酸アニオンを含む溶液（溶液１）を陽極誘電体層に塗布または浸漬する工程と、過硫酸塩を溶解した溶液（溶液２）を前後して別々に塗布または浸漬する工程を含んでもよい。また、溶液１及び溶液２の溶媒は同じでもよく、あるいは異なった溶媒系でもよい。

【００１３】

さらに前記酸化重合の繰り返し処理は、ハンダ耐熱性（熱安定性）の優れた固体電解質の生成を容易にする。従来既知のポリピロール等からなる固体電解質を用いたコンデンサでは、高温高湿度でのコンデンサ特性の変動が大きく信頼性を悪くしていたが、本発明で示された導電性組成物の固体電解質を具備したコンデンサは、熱安定性に優れかつドープ状態の安定性がよい。これは、前記２種以上のドーパントを有する重合体組成物が誘電体表面および細孔内部まで充填よく段階的に析出させることができるために、該重合体組成物の薄い膜質が何層にも重なった状態を作ることができる。これにより、該重合体が誘電体皮膜に対するダ

メージを生じない熱安定性に優れたコンデンサを提供することができる。

【0014】

次に重合反応の好ましい条件を以下に示す。

本発明のコンデンサの製造方法において用いられる一般式（II）の単量体濃度は、その化合物の置換基（種類）や溶媒等の種類によって異なるが、一般には１０$^{-3}$～１０モル／リットルの範囲が望ましく、１０$^{-2}$～５モル／リットルの範囲がさらに好ましい。また、反応温度は、それぞれ反応方法によって定められるもので特に限定できるものでないが、一般的には－７０℃～２５０℃の温度範囲で選ばれる。望ましくは、０℃～１５０℃であり、さらに１５～１００℃の温度範囲で行われることが好ましい。

【0015】

前記本発明の製造方法において用いられる溶液の溶媒は、例えばテトラヒドロフラン（ＴＨＦ）やジオキサン、ジエチルエーテル等のエーテル類、あるいはアセトン、メチルエチルケトン等のケトン類、ジメチルホルムアミドやアセトニトリル、ベンゾニトリル、Ｎ－メチルピロリドン（ＮＭＰ）、ジメチルスルホキシド（ＤＭＳＯ）等の非プロトン性極性溶媒、酢酸エチルや酢酸ブチル等のエステル類、クロロホルムや塩化メチレン等の非芳香族性の塩素系溶媒、ニトロメタンやニトロエタン、ニトロベンゼン等のニトロ化合物、あるいはメタノールやエタノール、プロパノール等のアルコール類、または蟻酸や酢酸、プロピオン酸等の有機酸または該有機酸の酸無水物（例、無水酢酸等）、水、あるいはこれらの混合溶媒を用いることができる。好ましくは、水、アルコール類、ケトン類および／またはその混合系が望ましい。

【0016】

このようにして製造された固体電解質の電導度は、０．１～２００Ｓ／ｃｍの範囲であるが、望ましい条件では１～１００Ｓ／ｃｍ、さらに好ましくは１０～１００Ｓ／ｃｍの範囲である。

【0017】

本発明の一方の電極にはアルミニウムまたはチタン、タンタル、ニオブあるいはこれらを基質とする合金系（等弁作用を有する）の箔、棒あるいはこれらを主

成分とする焼結体等の公知な材料が使用される。これらの金属電極表面は、比表面積を大きくする目的で公知な方法によってエッチング処理や化成処理されて金属箔上に該金属系酸化皮膜層を形成されたものが用いられる。

【0018】

固体電解質の形成は、誘電体層上で形成する方法が好ましく、とりわけ本発明の耐熱性の優れた有機系導電体を細孔あるいは空隙構造を有する誘電体上に化学的に析出する方法が好ましい。さらに、半導体上に電気的接触をよくするために導電体層を設けることが好ましく、例えば、導電ペーストの固体、またはメッキや、金属蒸着、導電樹脂フィルムの形成等が行われる。

【0019】

このように、本発明の製造方法から構成されるコンデンサは、例えば樹脂モールド、樹脂ケース、金属製の外装ケース、樹脂ディッピング等による外装により各種用途のコンデンサ製品とすることができる。

【0020】

【実施例】

以下、実施例及び比較例をあげて本発明を詳しく説明する。

（実施例１）

規定の面積に加工したアルミニウム化成箔を１０ｗｔ％のアジピン酸アンモニウム水溶液で１３Ｖ化成して、誘電体を準備した。この誘電体表面に、過硫酸アンモニウム（以下、ＡＰＳと略する）２０ｗｔ％と１－ナフタレンスルホン酸ナトリウム０．１ｗｔ％になるように調製した水溶液を含浸させ、次いで３，４－ジオキシエチレン－チオフェンを５ｇ溶解したイソプロパノール（以下ＩＰＡと略する）溶液に浸漬した。この基板を６０℃の環境下で１０分放置することで酸化重合を完成させ、水で洗浄した。この重合反応処理及び洗浄工程をそれぞれ１０回繰り返した。重合組成物中の硫酸イオン及び１－ナフタレンスルホン酸イオンの含量は、先ず前記重合組成物を水／ＩＰＡ溶媒中でヒドラジン還元して注意深く抽出し、イオンクロマトグラフィー法で求めたところ、硫酸イオン含量は重合体組成物の乾燥重量当り１．３重量％、１－ナフタレンスルホン酸イオン含量は、３３重量％であった。

【0021】

次に、ポリチオフェン重合体組成物を蓄積させたアルミニウム箔を、10wt%アジピン酸アンモニウム水溶液中で処理して、火花電圧について調べた。試験は、50℃環境下、電流密度10mA／cm^{2}の条件でn＝5回行ない、表1の結果を得た。次いで、陽極からの集電はアルミ芯部をプラス側リード端子に溶接することによって行ない、また陰極からの集電は、カーボンペーストと銀ペーストを介してマイナス側リード端子に接続し、最後にエポキシ樹脂で封止してコンデンサ素子を作製した。コンデンサ素子を125℃で2時間エージングした後に初期特性を測定した。これらの結果を表2にまとめた。ここで、表中、初期特性のCは容量を表わし、DFは損失角の正接（tanδ）を意味する。いずれも120Hzで測定したものである。インピーダンスは、共振周波数での値を示した。LC（漏れ電流）は、定格電圧を印加して1分後に測定した。各測定値は、試料数が30個の平均値であり、LCについては1μA以上をショート（不良）品として表示し、これを除いてLC値の平均を算出した。

【0022】

（実施例2）

実施例1で使用したAPSを過硫酸カリウムに替え、この濃度を10wt％とし、1－ナフタレンスルホン酸ナトリウム0．1wt％に調製された溶液に変更した以外は、実施例1の記載と同様であり、該コンデンサ素子を評価した。結果を表1、表2に示した。但し、重合組成物中の硫酸イオン及び1－ナフタレンスルホン酸イオンの含量は、実施例1記載の方法で求めたところ、硫酸イオン含量は2．1重量％、1－ナフタレンスルホン酸イオン含量は、29．5重量％であった。

【0023】

（実施例3）

実施例1で使用した20wt％のAPS濃度を35wt％に替え、また0．1wt％の1－ナフタレンスルホン酸ナトリウム濃度を0．04wt％に替えて水溶液を調製した以外は、実施例1の記載と同様であり、該コンデンサ素子を評価した。結果を表1、表2に示した。但し、重合組成物中の硫酸イオン及び1－ナ

フタレンスルホン酸イオンの含量は、実施例１記載の方法で求めたところ、硫酸イオン含量は４．７重量％、１－ナフタレンスルホン酸イオン含量は、９．５重量％であった。

【００２４】

（比較例１）

実施例１で使用したＡＰＳの替わりに硫酸鉄を１０ｗｔ％とし、１－ナフタレンスルホン酸ナトリウム０．１ｗｔ％に調製された溶液に変更した以外は、実施例１の記載と同様であり、該コンデンサ素子を評価した。結果を表１、表２に示した。但し、重合組成物中の硫酸イオン及び１－ナフタレンスルホン酸イオンの含量は、実施例１記載の方法で求めたところ、硫酸イオン含量は２０．５重量％、１－ナフタレンスルホン酸イオン含量は、３６．８重量％であった。しかしながら、鉄イオンが８重量％存在すること、および硫酸イオン含量が１０重量％以上よりも高いために、コンデンサ特性は悪かった。

【００２５】

（比較例２）

実施例１で使用したＡＰＳの替わりに塩化鉄を１０ｗｔ％とし、１－ナフタレンスルホン酸ナトリウム０．１ｗｔ％に調製された溶液に変更した以外は、実施例１の記載と同様であり、該コンデンサ素子を評価した。結果を表１、表２に示した。但し、重合組成物中の１－ナフタレンスルホン酸イオンの含量は、実施例１記載の方法で求めたところ、４．５重量％であった。硫酸イオンが併用して含有されていないためにコンデンサ特性は悪かった。

【００２６】

（比較例３）

実施例１記載の３，４－ジオキシエチレン－チオフェンをチオフェンに替えた以外は実施例１記載の条件と同じにして、コンデンサ素子を作製する処理を行った。しかし、黒青色のポリチオフェン重合体は全く生成せず、チオフェンの重合がＡＰＳの作用では起こらなかった。すなわち、ＡＰＳによるチオフェン類の酸化重合は、３，４－ジオキシ基置換のチオフェン類に対して特異的に起こった。

【００２７】

実施例１～３での火花電圧試験では、初期の電圧低下は大きいものの反応終了時の火花電圧はいずれも２７Ｖ以上であった。しかし、比較例１の硫酸鉄を用いた場合は、鉄イオンが８重量％も残存するために火花電圧の低下が大きく、規定の反応終了前に火花電圧が低下し、固体電解質の充填が不十分なままで終了し、好ましくなかった。

【００２８】

【表１】

火花電圧　　　(単位；Ｖ，ｎ＝５)

反応回数	実施例			比較例	
	１	２	３	１	２
１				２９	２５
２	３２	３５	３２	２５	２０
３				２２	１６
４	２９	３１	２８	２１	２
５				９	
６	２９	３０	２８	３	
８	２８	２９	２８		
１０	２８	２９	２８		

【００２９】

【表２】

	初期特性					
	Ｃ μＦ	ＤＦ ％	Ｚ mΩ	ＬＣ μＡ	不良数／試料数 個／個	ショート
実施例１	５．３	０．８	１５	０．０３	０／３０	０
実施例２	５．０	０．９	２１	０．０４	２／３０	０
実施例３	５．２	０．７	２３	０．０６	１／３０	０
比較例１	４．７	１．８	６５	０．０３	１６／３０	９
比較例２	４．０	３．４	３５５	０．４５	２８／３０	１７

【００３０】

【発明の効果】

固体電解質の導電性ポリチオフェン組成物に特定構造のポリチオフェンを使用し、かつ硫酸イオン含量が０．１～１０重量％の範囲であり、かつナフタレンス

ルホン酸イオン含量が１～５０重量％の範囲に制御することによって、該固体電解質を具備した固体電解コンデンサの耐電圧特性（火花電圧試験）、高周波特性、ｔａｎδ、インピーダンス特性、漏洩電流、耐熱性（リフロー性）等が大幅に向上する効果を見い出した。

【書類名】　要約書

【要約】

【課題】　耐電圧特性、高周波特性、ｔａｎδ、漏洩電流、耐熱性（リフロー性）等の優れた固体電解コンデンサを提供する。

【解決手段】　弁作用金属上に形成した酸化皮膜層表面に導電性ポリチオフェン組成物を形成してなる固体電解コンデンサにおいて、特定構造のポリチオフェンを使用し、かつ固体電解質中の硫酸イオン含量が０．１～１０重量％の範囲であり、かつナフタレンスルホン酸イオン含量が１～５０重量％の範囲に制御することによって、特に耐電圧特性の優れた固体電解コンデンサを製造する。

【選択図】　なし

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APPLICATION NUMBER	FILING/RECEIPT DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO./TITLE
60/106,969	11/04/98	KONUMA	H

#3

SUGHRUE MION ZINN MACPEAK & SEAS
2100 PENNSYLVANIA AVENUE NW
WASHINGTON DC 20037-3202

NOT ASSIGNED

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DATE MAILED: 11/30/98

NOTICE TO FILE MISSING PARTS OF PROVISIONAL APPLICATION

Filed Under 37 CFR 1.53 (c)
Filing Date Granted

An Application Number and Filing Date have been assigned to this Provisional Application. The items indicated below, however, are missing. Applicant is given TWO MONTHS FROM THE DATE OF THIS NOTICE within which to file all required items and pay fees required below to avoid abandonment. Extensions of time may be obtained by filing a petition accompanied by the extension fee under the provisions of 37 CFR 1.136(a). **If any of items 1 or 2 are indicated as missing, the SURCHARGE set forth in 37 CFR 1.16(l) of ☐ $25.00 for a small entity in compliance with 37 CFR 1.27, or ☐ $50.00 for a non-small entity, must also be timely submitted in reply to this NOTICE to avoid abandonment.**

If all required items on this form are filed within the period set below, the total amount owed by applicant as a ☐ small entity (statement filed) ☐ non-small entity is $ 130

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- ☐ missing.
- ☐ insufficient.

Applicant must submit $______ to complete the basic filing fee and/or file a small entity statement claiming such status (37 CFR 1.27).

☐ 2. The provisional application cover sheet under 37 CFR 1.151(c)(1) is required identifying:
- ☐ either the city and state or city and foreign country of the residence of each inventor.
- ☐ the title of the invention.

☒ 3. The application was filed in a language other than English.
Applicant must file a verified English translation of the application, the $130.00 set forth in 37 CFR 1.17(k), unless previously submitted, and a statement that the translation is accurate (37 CFR 1.52(d)).

☐ 4. A $50.00 processing fee is required since your check was returned without payment (37 CFR 1.21 (m)).

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DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/106,969 filed on November 4, 1998.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 20th day of January, 1999

Atsuko Ikeda

Atsuko Ikeda

[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

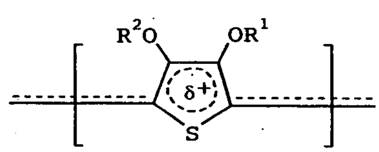
Solid Electrolytic Capacitor and Method for Producing the Same

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A solid electrolytic capacitor comprising a valve acting metal anode foil having formed on the surface thereof an oxide dielectric film, and a solid electrolyte formed by providing an electrically conducting polythiophene composition on the metal foil, wherein said composition has a sulfate ion content of from 0.1 to 10 wt% and a naphthalenesulfonate ion content of from 1 to 50 wt%.

[Claim 2] The solid electrolytic capacitor as claimed in claim 1, wherein the electrically conducting polythiophene composition contains a structural unit represented by the following formula (I):

[Chem. 1]



(I)

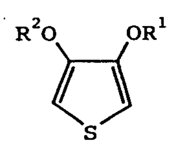
(wherein the substituents R^1 and R^2 each independently represents hydrogen, a linear or branched, saturated or unsaturated alkyl group having from 1 to 6 carbon atoms or a substituent for forming at least one 5-, 6- or 7-membered

saturated hydrocarbon ring structure containing the two oxygen elements shown in the formula by combining the hydrocarbon groups each having from 1 to 6 carbon atoms to each other at an optional site, said ring structure formed includes a chemical structure such as a substituted vinylene group and a substituted o-phenylene group in the scope thereof, and δ is a number of from 0 to 1).

[Claim 3] The solid electrolytic capacitor as claimed in claim 1, wherein the sulfate ion is originated in a reductant of a persulfate.

[Claim 4] A method for producing a solid electrolytic capacitor, comprising providing an electrically conducting polythiophene composition as a solid electrolyte on a valve acting metal anode foil having formed on the surface thereof an oxide dielectric film, wherein said solid electrolyte is produced by oxidation-polymerizing a thiophene monomer represented by the following formula (II):

[Chem. 2]



(II)

(wherein R^1 and R^2 are the same as defined in claim 1) by the action of a persulfate in the coexistence of a

naphthalenesulfonate anion.

[Claim 5] The method for producing a solid electrolytic capacitor as claimed in claim 4, wherein the persulfate is ammonium persulfate or potassium persulfate.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a solid electrolytic capacitor having excellent voltage withstanding property and a production method thereof. More specifically, the present invention relates to a production method of a solid electrolytic capacitor, wherein the solid electrolyte is produced by polymerizing a specific thiophene compound using a persulfate as an oxidizing agent in the coexistence of a naphthalenesulfonate anion, and to the capacitor.

[0002]

[Background Art]

A solid electrolytic capacitor comprises an anode substrate comprising a metal foil subjected to etching treatment and having a large specific surface area. A basic device of the capacitor is manufactured by forming an oxide dielectric film layer on the anode substrate, a solid semiconductor layer (hereinafter simply referred to as a solid electrolyte) as an opposing electrode outside the dielectric layer and preferably further an electric

conductor layer such as an electrically conducting paste. Then, the device as a whole is completely sealed by an epoxy resin or the like and put into use as a capacitor part in electric products over a wide range.

[0003]

Of these basic elements, for the solid electrolyte, it has been heretofore known to use, for example, an inorganic semiconductor material such as manganese dioxide and lead dioxide, a TCNQ complex salt, an intrinsic electrically conducting polymer having an electric conductivity of from 10^{-3} to 5×10^{3} S/cm (JP-A-1-169914 (the term "JP-A" as used herein means an "unexamined published Japanese patent application")) or a π-conjugated polyaniline (JP-A-61-239617), polypyrrole (JP-A-61-240625) or polythiophene derivative (JP-A-2-15611).

[0004]

[Problems to Be Solved by the Invention]

As the method for forming a solid electrolyte layer, a method of forming by fusion a solid electrolyte layer on a dielectric layer of a valve acting metal surface having a porous or void structure, and a method of producing a solid electrolyte on a dielectric layer have been conventionally known. For example, in the case of using a polymer of a 5-membered heterocyclic compound such as pyrrole or thiophene, a method where an anode foil is dipped in a solution

obtained by dissolving a 5-membered heterocyclic compound in a solution comprising a lower alcohol and water, and then dipped in an aqueous solution having dissolved therein an oxidizing agent and an electrolyte to give rise to chemical polymerization, thereby forming an electrically conducting compound (JP-A-5-175082), and a method where a 3,4-dioxyethylenethiophene monomer and an oxidizing agent each preferably in the form of a solution are applied separately differing in time or simultaneously on an oxide forming a layer of a metal foil to thereby form a solid electrolyte layer (JP-A-2-15611) are known.

[0005]

Known examples of the oxidizing agent which can be used in the chemical polymerization of a 5-membered heterocyclic compound such as thiophene include iron(III) chloride, $Fe(ClO_4)_3$, organic acid iron(III), inorganic acid iron(III), alkylpersulfate, ammonium persulfate (hereinafter simply referred to as "APS"), hydrogen peroxide and $K_2Cr_2O_7$ (see, JP-A-2-15611).

[0006]

[Means to Solve the Problems]

However, the capacitor comprising a solid electrolyte of the manganese dioxide is disadvantageous in that the oxide film layer is ruptured at the thermal decomposition of manganese nitrate and the impedance property is not

satisfactory. Use of lead dioxide is accompanied with a fear of adverse effect on the environment and not preferred. The solid electrolyte capacitor using a TCNQ complex salt has good heat fusion workability and excellent electric conductivity but the TCNQ complex salt itself has a problem in the heat resistance and in turn, the soldering heat resistance is poorly reliable. In order to overcome these problems, an electrically conducting polymer such as polypyrrole is applied to the solid electrolyte on a dielectric surface by electrochemical polymerization or chemical polymerization but satisfactory results cannot be obtained with respect to the homogeneity of film, soldering heat resistance, impedance property and the like.

As such, not only selection of a material for the solid electrolyte but also control of heat stability of the electric conductivity, homogeneity of the film and the like are important in producing a capacitor device in practice. In the chemical polymerization of thiophenes, the kind and residual amount of an oxidizing agent, the residual amount of a reductant of the oxidizing agent, the content of another anion having a dopant ability, the method for cleaning the residual monomer and the like are also important technical matters to be solved.

[0007]

[Mode for Carrying Out the Invention]

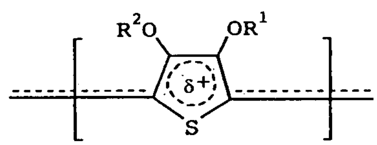
The object of the present invention is to produce a solid electrolytic capacitor having excellent properties satisfying the requirements with respect to the highest reduction in the weight, high capacity, high frequency property, tan δ, leakage current, heat resistance (reflow property) and durability. As a result of extensive investigations on the kind of the oxidizing agent, the residual amount of a reductant of the oxidizing agent and the content of an anion species having a dopant ability, the above-described object can be attained by a solid electrolytic capacitor comprising a valve acting metal anode foil having formed on the surface thereof an oxide dielectric film, and a solid electrolyte formed by providing an electrically conducting polythiophene composition on the metal foil, wherein the composition has a sulfate ion content of from 0.1 to 10 wt% and a naphthalenesulfonate ion content of from 1 to 50 wt%, as well as by a production method thereof. According to the present invention, a capacitor having excellent voltage withstanding property in addition to the objective required capabilities can be produced.

[0008]

More specifically, the present invention provides a

solid electrolytic capacitor characterized in that the above-described electrically conducting polythiophene composition contains a structural unit represented by the following formula (I):

[Chem. 3]



(I)

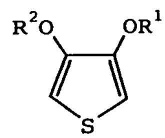
(wherein the substituents R^1 and R^2 each independently represents hydrogen, a linear or branched, saturated or unsaturated alkyl group having from 1 to 6 carbon atoms or a substituent for forming at least one 5-, 6- or 7-membered saturated hydrocarbon ring structure containing the two oxygen elements shown in the formula by combining the hydrocarbon groups each having from 1 to 6 carbon atoms to each other at an optional site, the ring structure formed includes a chemical structure such as a substituted vinylene group and a substituted o-phenylene group in the scope thereof, and δ is a number of from 0 to 1).

[0009]

The solid electrolytic capacitor is characterized in that in the method of producing a solid electrolytic capacitor comprising a solid electrolyte formed by providing an electrically conducting polythiophene

composition, the solid electrolyte is produced by oxidation-polymerizing a thiophene monomer represented by the following formula (II):

[Chem. 4]



(II)

(wherein R^1 and R^2 are the same as defined in the formula (I)) by the action of a persulfate in the coexistence of a naphthalenesulfonate anion. By having such characteristic features, a solid electrolytic capacitor having excellent voltage withstanding property and low impedance can be produced and thus, the present invention has been accomplished.

[0010]

The present invention is described in detail below.

In the above-described production method, opposing electrodes are used, a dielectric layer comprising a metal oxide fine structure is provided on the surface of one electrode and an electrically conducting polymer composition obtained by chemically polymerizing a specific thiophene represented by formula (II) is provided as a solid electrolyte on the dielectric layer. In formula (II), the substituents R^1 and R^2 each independently represents

hydrogen or a linear or branched, saturated or unsaturated alkyl group having from 1 to 6 carbon atoms, and the substituents each is preferably methyl, ethyl, propyl, isopropyl, vinyl or allyl. The hydrocarbon groups each having from 1 to 6 carbon atoms of R^1 and R^2 may be combined at any site to each other to form at least one 5-, 6- or 7-membered saturated hydrocarbon ring structure containing the two oxygen elements shown in formula (II), and preferred examples thereof include 1,2-ethylene, 1,2-propylene and 1,2-dimethylethylene. Furthermore, the hydrocarbon groups each having from 1 to 6 carbon atoms of R^1 and R^2 may be combined at any site to each other to form an unsaturated hydrocarbon ring structure such as substituted vinylene group and substituted o-phenylene group, and examples thereof include 1,2-vinylene, 1,2-propenylene, 2,3-butylen-2-ene, 1,2-cyclohexylene, methyl-o-phenylene, 1,2-dimethyl-o-phenylene and ethyl-o-phenylene.

[0011]

Out of thiophenes represented by formula (II) for use in the production method of the present invention, a part of monomer compounds including 3,4-dioxyethylene-thiophene are already known (see, JP-A-2-15611). Furthermore, out of the persulfates as the oxidizing agent for use in the present invention, use of ammonium persulfate (hereinafter simply referred to as "APS") or alkali metal persulfate is

also known.

However, in the present invention, the electrically conducting composition has a sulfate ion content of from 0.1 to 10 wt%, preferably from 0.2 to 5 wt%, and a naphthalenesulfonate ion content of from 1 to 50 wt%, preferably from 5 to 40 wt%, and at the same time contains a structural unit represented by the formula (I). A solid electrolytic capacitor comprising a solid electrolyte formed of a polymer of this electrically conducting composition has particularly excellent voltage withstanding property and this has hitherto been not known. In the present invention, the total of the sulfate ion content and the naphthalenesulfonate ion content is preferably from 1.1 to 60 wt% based on the entire weight of the electrically conducting composition.

[0012]

Usually, the method for forming the above-described solid electrolyte plays an important role in the production of a capacitor for attaining high capacity and high frequency property and improving tan δ, leakage current, heat resistance (reflow property) and durability. More specifically, it is important to form a densely filled solid electrolyte and thereby improve the homogeneity of the electric conducting path. To this effect, the constitution of the electrically conducting composition has

a great effect on the capacity properties. In the present invention, the process of oxidation-polymerizing the above-described thiophene monomer by the action of a persulfate in the coexistence of a naphthalenesulfonate anion to produce the solid electrolyte is performed in a plurality of repetitions, preferably from 5 to 20 repetitions to an anode substrate and thereby an objective solid electrolyte can be easily obtained. In this process, a step where the anode dielectric layer is coated with or dipped in a solution containing the above-described thiophene monomer and naphthalenesulfonate anion (Solution 1) may be provided separately before or after a step where the layer is coated with or dipped in a solution having dissolved therein a persulfate (Solution 2). Solution 1 and Solution 2 may use the same solvent or may differ in the solvent system.

[0013]

By repeating the oxidation-polymerization process, a solid electrolyte having excellent soldering heat resistance (heat stability) can also be easily produced. In conventionally known capacitors using a solid electrolyte comprising polypyrrole or the like, the capacitor properties greatly fluctuate at a high temperature and a high humidity and the reliability is low. On the other hand, the capacitor comprising a solid electrolyte formed of an electrically conducting composition of the present

invention has excellent heat stability and exhibits good stability in the doped state, because the polymer composition having two or more dopants can be thoroughly filled step by step into the dielectric surface, even inside the pore, and thereby a structure where many thin films of the polymer composition are overlaid one on another can be formed. As a result, the polymer can prevent damages of the dielectric film and a capacitor having excellent heat stability can be provided.

[0014]

Preferred conditions for the polymerization reaction are described below.

The concentration of the monomer represented by formula (II) for use in the production method of a capacitor of the present invention varies depending on the substituent (kind) of the compound or the kind of solvent, however, it is in general preferably from 10^{-3} to 10 mol/ℓ, more preferably from 10^{-2} to 5 mol/ℓ. The reaction temperature is selected according to respective reaction processes and cannot be specifically limited, however, it is generally from -70 to 250°C, preferably from 0 to 150°C and more preferably from 15 to 100°C.

[0015]

Examples of the solvent for use in the production method of the present invention include tetrahydrofuran

(THF), dioxane, ethers such as diethyl ether, ketones such as acetone and methyl ethyl ketone, aprotic polar solvents such as dimethylformamide, acetonitrile, benzonitrile, N-methylpyrrolidone (NMP) and dimethylsulfoxide (DMSO), esters such as ethyl acetate and butyl acetate, nonaromatic chlorine-type solvents such as chloroform and methylene chloride, nitro compounds such as nitromethane, nitroethane and nitrobenzene, alcohols such as methanol, ethanol and propanol, organic acids such as formic acid, acetic acid and propionic acid, acid anhydrides of the organic acid (e.g., acetic anhydride), water, and a mixed solvent thereof. Of these, preferred are water, an alcohol, a ketone and/or a combination thereof.

[0016]

The solid electrolyte thus produced has an electric conductivity of from 0.1 to 200 S/cm, preferably from 1 to 100 S/cm, more preferably from 10 to 100 S/cm.

[0017]

In the present invention, for one part electrode, a known material such as aluminum, titanium, tantalum, niobium, an alloy (having the same valve action) using such a material as a substrate or a sintered body mainly comprising such a material, is used in the form of a foil or bar. This metal electrode is used after treating the surface thereof by a known method such as etching or

chemical forming treatment so as to increase the specific surface area, and thereby forming a metal oxide film layer on the metal foil.

[0018]

The solid electrolyte is preferably formed by effecting the formation process on the dielectric layer. In particular, a method of chemically depositing an organic electric conductor having excellent heat resistance of the present invention on a dielectric material having a porous or void structure is preferred. Furthermore, in order to attain good electrical contacting, an electric conductor layer is preferably provided on the semiconductor and the electrical conductor layer is formed, for example, by solidifying an electrically conducting paste, plating, sputtering a metal or forming an electrically conducting resin film.

[0019]

The capacitor thus constituted according to the production method of the present invention is jacketed with a resin mold, a resin case or a metal-made jacket case or by resin dipping and then the capacitor can be used as a product capacitor for various uses.

[0020]

[Examples]

The present invention is described in greater detail

below by referring to the Examples and Comparative Examples.

(Example 1)

An formed aluminum foil was processed to have a prescribed area and then subjected to formation at 13 V in an aqueous 10 wt% ammonium adipate solution to prepare a dielectric material thereon. The surface of this dielectric material was impregnated with an aqueous solution prepared to have an ammonium persulfate (hereinafter simply referred to as "APS") concentration of 20 wt% and a sodium 1-naphthalenesulfonate concentration of 0.1 wt%, and then the dielectric material was dipped in an isopropanol (hereinafter simply referred to as "IPA") solution having dissolved therein 5 g of 3,4-dioxyethylene-thiophene. The resulting substrate was left standing in an environment at 60°C for 10 minutes, thereby completing the oxidation polymerization, and then washed with water. This polymerization reaction and washing process each was repeated 10 times. The polymer composition was reduced by hydrazine in a water/IPA solvent and then carefully extracted with the solvent and the contents of sulfate ion and 1-naphthalenesulfonate ion in the polymer composition were determined by an ion chromatography method. As a result, the sulfate ion content was 1.3 wt% and the 1-naphthalenesulfonate ion content was 33 wt%, based on the dry weight of the polymer composition.

[0021]

Thereafter, an aluminum foil having accumulated thereon the polythiophene polymer composition was treated in an aqueous 10 wt% ammonium adipate solution and then examined on the sparking voltage. The test was performed in an environment of 50°C under the conditions of a current density of 10 mA/cm^2 at n=5. The results obtained are shown in Table 1. Subsequently, the aluminum core part was welded with a plus side lead terminal for collecting the current from the anode and on the other hand, connected to the minus side lead terminal through carbon paste and silver paste for collecting the current from the cathode. These elements were sealed by an epoxy resin to manufacture a capacitor device. The capacitor device manufactured was aged at 125°C for 2 hours and then determined on the initial characteristics. The results obtained are shown together in Table 2. In the Table, C in the column of initial characteristics indicates a capacity and DF indicates a tangent (tan δ) of the loss angle. These were each measured at 120 Hz. The impedance is shown by a value at a resonance frequency. LC (leakage current) was measured one minute after application of a rated voltage. The measured values each is an average of 30 samples. With respect to LC, those having an LC of 1 μA are judged as a shorted product (defective) and the average LC is calculated exclusive of

the defective units.

[0022]

(Example 2)

A capacitor device was prepared and evaluated in the same manner as in Example 1 except for using potassium persulfate in place of APS used in Example 1 and preparing a solution having a potassium sulfate concentration of 10 wt% and a sodium 1-naphthalenesulfonate concentration of 0.1 wt%. The results obtained are shown in Tables 1 and 2. The contents of sulfate ion and 1-naphthalenesulfonate ion in the polymer composition were determined by the method described in Example 1 and it was found that the sulfate ion content was 2.1 wt% and the 1-naphthalenesulfonate ion content was 29.5 wt%.

[0023]

(Example 3)

A capacitor device was prepared and evaluated in the same manner as in Example 1 except for preparing a solution by changing the concentration of APS used in Example 1 from 20 wt% to 35 wt% and the concentration of sodium 1-naphthalenesulfonate from 0.1 wt% to 0.04 wt%. The results obtained are shown in Tables 1 and 2. The contents of sulfate ion and 1-naphthalenesulfonate ion in the polymer composition were determined by the method described in Example 1 and it was found that the sulfate ion content was

4.7 wt% and the 1-naphthalenesulfonate ion content was 9.5 wt%.

[0024]

(Comparative Example 1)

A capacitor device was prepared and evaluated in the same manner as in Example 1 except for using ferric sulfate in place of APS used in Example 1 and preparing a solution having a ferric sulfate concentration of 10 wt% and a sodium 1-naphthalenesulfonate concentration of 0.1 wt%. The results obtained are shown in Tables 1 and 2. The contents of sulfate ion and 1-naphthalenesulfonate ion in the polymer composition were determined by the method described in Example 1 and it was found that the sulfate ion content was 20.5 wt% and the 1-naphthalenesulfonate ion content was 36.8 wt%. Since 8 wt% of iron ion (ferric and ferrous ions) was also present and the sulfate ion content exceeded 10 wt%, the capacitor had poor properties.

[0025]

(Comparative Example 2)

A capacitor device was prepared and evaluated in the same manner as in Example 1 except for using ferric chloride in place of APS used in Example 1 and preparing a solution having a ferric iron chloride concentration of 10 wt% and a sodium 1-naphthalenesulfonate concentration of 0.1 wt%. The results obtained are shown in Tables 1 and 2.

The content of 1-naphthalenesulfonate ion in the polymer composition was determined by the method described in Example 1 and found to be 4.5 wt%. Since sulfate ion was not used in combination, the capacitor had poor properties.

[0026]

(Comparative Example 3)

A process for manufacturing a capacitor device was performed under the same conditions as in Example 1 except for using thiophene in place of 3,4-dioxyethylene-thiophene used in Example 1. However, black blue polythiophene polymer was not produced at all and thus, polymerization of thiophene was not caused by the action of APS. In other words, occurrence of the oxidation polymerization of a thiophene by APS was peculiar to 3,4-dioxy group-substituted thiophenes.

[0027]

In the sparking voltage test of Examples 1 to 3, the voltage was greatly reduced at the initial stage, however, at the completion of the reaction, the sparking voltage was 27 V or more in each Example. In Comparative Example 1 using ferric sulfate, the sparing voltage was largely reduced due to remaining of iron ion (ferric and ferrous ions) in a concentration as high as 8 wt% and the sparking voltage could not withstand until the prescribed reaction was completed. As a result, the solid electrolyte was

insufficiently filled and this was disadvantageous.

[0028]

[Table 1]

Sparking Voltage

(unit: V, n=5)

Number of Reaction Times	Example			Comparative Example	
	1	2	3	1	2
1				29	25
2	32	35	32	25	20
3				22	16
4	29	31	28	21	2
5				9	
6	29	30	28	3	
8	28	29	28		
10	28	29	28		

[0029]

[Table 2]

	Initial Characteristics					
	C μF	DF %	Z mΩ	LC μA	Number of Defective/Number of Sample units/units	Short Circuit
Example 1	5.3	0.8	15	0.03	0/30	0
Example 2	5.0	0.9	21	0.04	2/30	0
Example 3	5.2	0.7	23	0.06	1/30	0
Comparative Example 1	4.7	1.8	65	0.03	16/30	9
Comparative Example 2	4.0	3.4	355	0.45	28/30	17

[0030]

[Effect of the Invention]

By using a polythiophene having a specific structure for the electrically conducting thiophene compound of the solid electrolyte and controlling the sulfate ion content and the naphthalenesulfonate ion content to fall within the range of from 0.1 to 10 wt% and from 1 to 50 wt%, respectively, an effect is provided such that a solid electrolytic capacitor comprising the solid electrolyte is greatly improved in the voltage withstanding property (sparking voltage test), high frequency property, tan δ, impedance property, leakage current, heat resistance (reflow property) and the like.

[NAME OF DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To obtain a solid electrolytic capacitor having excellent properties with respect to the voltage withstanding property, high frequency property, tan δ, leakage current, heat resistance (reflow property) and the like.

[MEANS TO SOLVE THE PROBLEM]

A solid electrolytic capacitor comprising a valve acting metal, an oxide film layer formed on the metal and an electrically conducting polythiophene composition formed on the surface of the oxide film layer, wherein a polythiophene having a specific structure is used and the solid electrolyte has a sulfate ion content of from 0.1 to 10 wt% and a naphthalenesulfonate ion content of from 1 to 50 wt%. The solid electrolytic capacitor produced has excellent voltage withstanding property.

[SELECTED DRAWING] None.

ATTN: BOX PROVISIONAL PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Provisional Application of

KONUMA, Hiroshi; FURUTA, Yuji and SAKAI, Atsushi

Provisional Application No.: 60/106,969

Filed: November 4, 1998

For: SOLID ELECTROLYTIC CAPACITOR AND METHOD FOR PRODUCING THE SAME

SUBMISSION OF VERIFIED ENGLISH LANGUAGE TRANSLATION

BOX PROVISIONAL PATENT APPLICATION
Attn: Office of National Application Review
Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

In response to the "Notice to File Missing Parts of Provisional Application Filed Under 37 CFR 1.53(b)(2)", mailed November 30, 1998, submitted herewith is the verified English language translation (23 pages of specification) for the above-mentioned provisional application previously filed in the Japanese language.

A check for the statutory fee of $130.00 is attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. 1.16 and 1.17 which may be required during the entire pendency of the provisional application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Respectfully submitted,

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In re Application of: Konama et al

Application Number: 60/106969 | Filed: 11-4-04

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United States Patent Application Publication No. ______________, page, __________ line ________.

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